3-9051

McMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF METALLURGY AND MATERIALS SCIENCE

CONTRACT REPORT NO. OSU 83-00077

FINAL REPORT ON
STUDY OF SYNTHESIS OF NGS, NYS and BETA-ALUMINA

D.S.S. #20SU 23440-3-9051

APRIL 1983 - APRIL 1984

PATRICK S. NICHOLSON

Research Associates; K. Yamashita
Z. Munshi
Research Assistants: W. Gronau
E. Nicholson
S. Kamenshchik

17pp

for

Department of Energy, Mines and Resources

(Dr. A. Kuriakose - Scientific Authority)

June 1984

MICROMEDIA

PART I: McMaster Produced NGS and NYS Samples for CANMET

The chemicals were mixed in the following ratios. One part of 0.1M $Gd(OOCH_3)_3\ 4H_2O$ or $Y(NO_3)_3\ 8H_2O$ (Alfa Product), four parts of 0.1M Na_2SiO_3"GD" (National Silicates Ltd.) and 0.56 parts of 0.1M Na_2CO_3 (BDH Chemicals). All the chemicals were cooled in an ice water bath for 2-3 hours prior to mixing and spraying. The solution was spray-dried in a "Buchi" spray-dryer. The solution was stirred constantly to maintain the precipitates in suspension. The spray-dried yield of 1L-0.1M $Gd\ (OOCH_3)_3\ 4H_2O$ was 60-65 gms and 1L-0.1M $Y(NO_3)_3\ 6H_2O$ was 50 gms.

The NGS and NYS were calcined as follows:

NGS ..... 540°C/24 hrs.

NYS ..... 620°C/3.5 hrs.

The temperature was increased slowly (50°C/hr). The yield following calcination was 70-72%. Following calcination the powder was ball-milled overnight using teflon grinding media.

The powder was uniaxially pressed into pellets, discs and bars at 3000 psi. The shapes were subsequently isopressed in condoms at 40-50 Kpsi. Sintering was conducted in a "Pottery Supply House" furnace under the following conditions,

NGS ..... 1050°C/25 mins.

NYS ..... 1125°C/22 mins.

These conditions are requisite to produce single-phase sintered NGS and NYS. During sintering, all samples were covered by an atmosphere of their own powder. Density measurements were conducted on all samples using the liquid immersion technique. X-ray diffraction analysis was used to determine the phase composition of the sinter. The results are shown in Tables I and II. All the samples were given to CANMET.

Table 1

NYS

Sample #	Isopress Kpsi	Green density %theor.	Sintered density %theor.	f(NYS)
1.	37	57.28	100	98-100
2.	37	58.12	100	"
3.	37	57.52	100	"
4.	37	57.78	99.9	"
5.	52	58.64	100	"
6.	52	59.14	100	"
7.	52	59.54	100	"
8.	52	59.21	100	"
9.	52	59.64	100	"
10.	52	59.52	99.9	"
11.	52	59.85	100	"
12.	52	59.69	100	"
13.	52	59.41	100	"
14.	52	59.62	98.37	"
15.	52	59.35	100	"
16.	52	58.73	100	"
17.	52	59.62	100	"
18.	52	60.09	100	"
19.	52	59.80	100	"
20.	52	60.48	100	"
21.	49	59.21	100	"
22.	49	58.61	100	"
23.	49	59.45	100	"

Table 1 Contd.

NYS

Sample #	Isopress Kpsi	Green density %theor.	Sintered density %theor.	f(NYS)
24.	49	58.24	100	98-100
25.	49	58.97	100	"
27.	49	57.27	96.7	"
28.	49	57.51	97.99	"
29.	49	56.79	97.90	"
30.	45	56.94	97.7	"
31.	45	55.77	98.15	"
Bars				
1.	46	56.1	99.2	"
2.	46	55.8	98.89	"
Discs				
1.	46	57.60	97.92	"
2.	46	56.48	99.32	"
3.	46	56.4	97.02	"

Table 11

NGS

Sample #	Isopress Kpsi	Green density %theor.	Sintered density %theor.	f(NGS)
1.	50	56.12	94.48	98-100%
2.	50	56.22	93.1	"
3.	50	56.7	97.33	"
4.	50	56.26	97.15	"
5.	50	60.96	94.90	"
6.	50	61.29	94.05	"
7.	50	61.81	94.17	"
8.	50	61.34	95.44	"
9.	37	54.08	94.98	"
10.	37	53.57	94.44	"
11.	37	53.8	94.16	"
12.	37	52.71	95.05	"
13.	37	53.06	93.5	"
14.	37	57.2	94.74	"
15.	37	52.78	93.75	"
16.	37	52.92	94.54	"
17.	37	53.09	95.64	"
18.	37	53.6	96.45	"
19.	37	54.06	95.36	"
20.	37	54.54	97.08	"
21.	37	53.09	94.92	"
22.	37	53.75	93.3	"
23.	50	56.49	94.68	"

Table 11 Continued

NGS

Sample #	Isopress Kpsi	Green density %theor.	Sintered density %theor.	f(NGS)
24.	37	57.73	95.29	98-100%
25.	50	56.47	94.54	"
26.	50	55.43	94.84	"
27.	50	55.96	93.63	"
28.	49	55.46	93.9	"
29.	49	56.03	93.83	"
30.	49	56.65	94.6	"
31.	47	56.1	94.1	"
32.	47	55.46	93.3	"
33.	47	56.03	93.91	"
Bars 1.	43	53.31	94.81	"
2.	43	54.25	94.98	"
Discs 1.	43	56.37	93.85	"
2.	43	53.36	95.02	"
3.	43	56.68	95.4	"

PART II: McMaster Produced Sodium-Stabilized Potassium Beta Alumina for CANMET

Three compositions of sodium stabilized potassium beta alumina were made for CANMET. One was the basic composition and the other two slight variations of this. The chemicals were obtained from the following companies; $Al_2(SO_4)_3 18H_2O$ (Baker Chemicals & BDH), $MgSO_4$ (Baker Chemicals), K_2CO_3 (BDH) and Na_2CO_3 (Fisher Chemicals).

Using distilled, deionized water, the dry chemicals were mixed into solution using an automatic magnetic stirrer. The solution was subsequently spray-frozen in liquid nitrogen and freeze-dried for 3.5-4 days. The freeze-dried powder was ball-milled in rubber lined jars for 1.5 hours using alumina grinding media.

The powders were calcined at 1300°C for 4 hours in small alumina crucibles using a gas fired furnace. A second ball-milling for 5 hours was carried out followed by a sieving through a 110 mesh sieve.

The powder was uniaxially pressed into pellets at 1000 psi. The pellets were placed into condoms and isopressed at 45-50 Kpsi. Sintering was conducted in a "Lucifer" type furnace. Each pellet was covered with a potassium beta alumina powder to prevent soda loss. Sintering was carried out at 1615-1617°C for 2 minutes followed by an anneal at 1400°C for 2 minutes. The pellets were then allowed to cool with the furnace. The density of each pellet was measured using the liquid immersion technique. Using x-ray diffraction analysis, $f(\beta)$ was measured on most samples. Results are shown in Table III and IV.

The good pellets from the basic composition batch were placed in plastic bags containing a dessicant and sent to CANMET. Several pellets of the variation compositions were sent to CANMET but density and quality were poor. The scientific authority was notified of the poor results obtained for these batches.

TABLE III

Sodium-Stabilized Potassium Beta Alumina–Basic Composition.

Sample #	Isopress Kpsi	Green density gm/cc	Sinter temp. °C	Sinter time min.	Sinter density % theoret.	f(β)
1.	50	1.62	1614-16	2	98.2	0.3-0.4
2.	50	1.63	1616-17	2	98.8	0.32
3.	50	1.66	1615-16	2	98.4	-
4.	50	1.66	1615-16	2	97.0	0.3-4
5.	50	1.67	1615-17	2	97.6	0.3-4
6.	50	1.66	1615-16	2	97.0	0.3-4
7.	45	1.67	1616-17	2	97.4	0.3-4
8.	45	1.67	1616-17	2	97.8	0.3-4
9.	45	1.63	1615-16	2	97.0	-
10.	45	1.63	1615-16	2	97.2	-
11.	45	1.63	1615-16	2	96.9	-
12.	45	1.62	1615-16	2	97.0	-
13.	45	1.63	1615-16	2	97.5	-
14.	45	1.66	1615-16	2	96.3	0.4-5
15.	45	1.67	1616-17	2	93.7	0.4-5
16.	45	1.66	1617-18	2	96.8	0.4-5
17.	45	1.66	1617-18	2	97.0	0.4-5
18.	45	1.67	1617-18	2	97.6	0.4-5
19.	45	1.57	1617-18	2	97.1	0.4-5
20.	45	1.59	1617-18	2	96.9	-
21.	45	1.57	1617-18	2	94.0	-
22.	45	1.60	1617-18	2	89.8	-
23.	50	1.66	1615-16	2	98.0	-
24.	50	1.62	1616-17	2	98.2	-
25.	45	1.63	1616-17	2	98.3	-
26.	50	1.66	1615-16	2	98.1	0.3-4
27.	50	1.62	1615-16	2	98.3	0.33
28.	50	1.63	1614-16	2	98.4	0.35
29.	50	1.62	1615-16	2	98.8	-
30.	45	1.59	1616-17	2	97.4	-

TABLE IV

Sodium-Stabilized Potassium Beta Alumina–Variation of Basic Composition

Sample #	Isopress Kpsi	Sinter temp. °C	Sinter time mins.	Sinter density % theoret.	Remarks
1.	45	1616-17	2	94.5	cracked
2.	45	1616-17	2	95.3	?cracks
3.	45	1616-17	2	94.2	cracked
4.	45	1615-16	2	90.8	
5.	45	1615-16	2	90.5	
6.	45	1615-16	2	91.2	
7.	45	1615-16	2	93.7	?cracks
8.	45	1615-16	2	90.7	
9.	50	1615-16	2	91.4	
10.	50	1615-16	2	92.3	
11.	50	1615-16	2	86.4	
12.	50	1615-16	2	87.2	
13.	45	1616-17	2	86.3	
14.	45	1617-18	2	86.0	
15.	50	1617-18	2	86.3	
16.	50	1617-18	2	73.9	cracking
17.	45	1615-16	2	86.4	
18.	45	1615-16	2	86.4	"
19.	50	1615-16	2	86.3	
20.	50	1615-16	2	85.1	
21.	45	1615-16	2	88.2	
22.	45	1616-17	2	85.4	
23.	50	1615-16	2	84.8	

PART III: CANMET Produced β/β" Alumina Powders

Three samples of CANMET spray-dried β/β" alumina powder were put through the McMaster processing procedure for hydronium superionic conductor precursor ceramics. 10 gms each of the following powders were received; 60NMSD, 60 NMLCSD and 60 NMLASD.

All three powders were ball-milled in rubber lined jars for 1.5 hours using Al_2O_3 grinding media. Each powder was then calcined for 4 hours at 1300°C, in small crucibles using a gas fired furnace. After calcination, the powder was weighed and the results are summarized in Table V. All powders were stored in a dessicator. It was noted however that, after calcination, 60 NMSD appeared to have partially sintered and the remaining powders were more coarse than the McMaster type. All powders were again ball-milled for 5 hours and screened through a 110 mesh sieve.

Two sizes of discs were attempted, i.e., 2.5 cm diameter and 1 cm diameter. The larger discs would not hold together without using a binder and as this is not normal procedure, no binder was added. It is thought that the powders may have been too coarse for the larger type discs. The smaller discs were successfully pressed using a "Carver" type press at a pressure of 1000 psi. The samples were then placed in condoms and isopressed at 35-40 Kpsi. All samples were stored in the dessicator until ready for sintering. A summary of this phase is in Table V.

All samples were sintered in a Lucifer elevator type furnace at 1615-17°C for 2 mins. Each sample was covered in a similar powder produced at McMaster to reduce soda loss on sintering. The samples were annealed at 1400°C for 2 mins., then allowed to cool with the furnace. Using tweezers and gloved hands, the density of each sample was measured using liquid immersion. A theoretical density of 3.25 cm^2/gm was used to calculate the density. The results are shown in Table VI.

TABLE V

	60NMSD	60NMLCSD	60NMLASD
Initial Wt.	10gms	10gms	10gms
Ball-mill# 1			
time	1.5hrs	1.5hrs	1.5hrs
#balls	50	50	50
Calcination			
Date	8/5/84	9/5/84	7/5/84
Time	4hrs	4hrs	4hrs
Temperature °C	1300	1300	1300
Remarks	Pwd.appeared partially sintered	Pwd.appeared coarse	Pwd. appeared coarse
Wt.after calcine	7gms	6gms	6gms
Ball-mill#2			
Date	9/5/84	10/5/84	8/5/84
Time	5hrs	5hrs	5hrs
#balls	35	35	35
Screening Remarks	Difficult to screen	More difficult than McMaster pwd.	More difficult than McMaster Pwd.
f(β) of calcined powder	0.28	0.46	0.44

ALL POWDERS WERE STORED IN PLASTIC BOTTLES INSIDE A DESSICATOR

TABLE V1

Results on CANMET Produced Powder Pellets

6ONLCSD

Pellet #	Uniaxial pressure psi	Isostatic pressure Kpsi	Green Density gm/cc	Sinter temp. °C	Sinter time mins.	Anneal temp. °C	Anneal time mins.	Density % theor.	Sinter f(β)	Remarks
1	1000	35	1.65	1616-17	2	1400	2	96.1	0.44	to exch.
2	1000	35	1.65	1616-17	2	1400	2	95.25	0.48	
3	1000	35	1.65	1616-17	2	1400	2	97.4	0.52	to exch.
4	1000	35	1.68	1615-16	2	1400	2	94.83	0.61	
5	1000	35	1.67	1616-17	2	1400	2	93.51	0.44	
6	1000	35	1.63	1616-17	2	1400	2	97.1	0.55	
7	1000	35	1.64	1616-17	2	1400	2	94.22	0.55	
8	1000	35	1.63	1615-16	2	1400	2	96.87	0.53	

6ONMSD

1	1000	40	1.62	1615-16	2	1400	2	90.48	0.52	to exch.
2	1000	40	1.67	1615-16	2	1400	2	87.45	0.48	
3	1000	40	1.66	1615-16	2	1400	2	87.92	0.49	
4	1000	40	1.64	1615-16	2	1400	2	90.12	0.44	
5	1000	40	1.65	1615-16	2	1400	2	88.47	0.59	to exch.
6	1000	40	1.65	1615-16	2	1400	2	cracked	0.47	
7	1000	40	1.63	1615-16	2	1400	2	82.46	0.47	
8	1000	40	1.67	1615-16	2	1400	2	83.38	0.44	
9	1000	40	1.66	1615-16	2	1400	2	84.30	0.44	

6ONMLASD

1	1000	35	1.85	1615-16	2	1400	2	91.07	0.44	
2	1000	35	1.80	1616-17	2	1400	2	95.38	0.44	
3	1000	35	1.81	1616-17	2	1400	2	97.53	0.62	to exch.
4	1000	35	1.73	1615-16	2	1400	2	cracked		
5	1000	35	1.81	1615-17	2	1400	2	92.3	0.51	to exch.
6	1000	35	1.81	1615-17	2	1400	2	89.23	o.44	to exch.

The f(β) of each sample was measured using an X-ray diffraction technique. Samples were polished slightly prior to this procedure to remove any residual powder after sintering. The results are shown in Table VI. All samples were stored in plastic envelopes with a dessicant and kept in a dessicator.

A pellet from each powder was subjected to the ion-exchange process to produce the hydrogen conducting analogue.

The following procedure was used:

- using a digital micrometer the sample dimensions were measured
- each sample was exchanged in a NaCl/KCl melt in two stages:-

  A, 0.5 : 0.5 KCl:NaCl at 800^{o}C

  B, 1.0 KCl at 800^{o}C

  Samples from each batch deteriorated, consequently a less vigorous potassium exchange process was carried out.

  A, 0.25 : 0.25 KCl:NaCl at 800^{o}C

  B, 0.5 : 0.5 KCl:NaCl at 800^{o}C
- after potassium exchange, the samples were washed to remove surface chlorides, dried at 200^{o}C then weighed.
- the samples proceded to the hydronium ion exchange and were attached to the unit with RTV silicone adhesive. H_2 gas enriched with Ar was bubbled just below the Pt. foil anode. Another Pt. foil acted as the cathode.

Conditions for this process were:

- 0.1M Acetic acid
- when thermal equilibrium ($\simeq$ 80^{o}C) was reached, a constant current of 1μA was allowed to pass through the solid electrolyte checked by a potentiostat.
- after 24 hours current passage was terminated. The samples were removed, washed and dried at 150^{o}C for 1 hour then weighed.
- Young's Modulus was measured on each sample before exchange, after potassium

exchange and again after hydronium exchange.

The exchange results are shown in Table VII. Both 60NMLCSD pellets deteriorated during the KCl exchange. Only two pellets remained intact after the hydronium exchange, 60NMLASD #5 and 60NMSD #1.

The values for Young's Modulus, longitudinal and shear velocity and Poisson's ratio are shown in Table VIII.

All samples, exchanged and otherwise, have been returned to CANMET.

TABLE V11

Powder #	60NMLCSD	60NMSD	60MLCSD	60NMLASD	60NMSD	60NMLASD
Pellet #	1	5	3	5	1	6
Sintered mean thickness/cm	0.2928	0.1890	0.2452	0.2317	0.1888	0.2246
Sintered mean diameter /cm	1.200	1.320	1.215	1.325	1.290	1.320
f(β)	0.44	0.59	0.52	0.51	0.52	0.44
Density before exchange/gcm $^{-3}$	3.12	2.88	3.17	3.00	2.94	2.90
Wt. before exchange/g	0.87885	0.52087	0.74873	0.76717	0.52472	0.73281
Wt. after KCl exchange/g	0.96523	0.64900	0.84403	0.86998	0.65101	0.81232
Thickness after KCl exchange/cm	-	0.1891	0.2471	0.2323	0.1895	0.2249
Diameter after KCl exchange/cm	-	1.327	1.219	1.329	1.295	1.323
Wt. after Hydronium exchange/g	-	-	-	0.74083	0.52307	0.71386
Thickness after Hydronium exch./cm	-	-	-	0.2330	0.1884	0.2277
Diameter after Hydronium exch./cm	-	-	-	1.331	1.288	1.327
Constant current during hydronium exch./μA	-	-	-	1	1	1
Constant current exch. time/hrs	-	-	-	24	24	24
Remarks	pellet crumbled in the KCl exch.	pellet cracked after KCl exch.	pellet cracked after KCl exch.	pellet intact	pellet intact	pellet cracked during washing

TABLE VIII

Sample		Before exchange	After K exchange	After H_3O^+ exchange
60NMSD #1	VL/ms^{-1}	-	-	5488
	VS/ms^{-1}	-	-	3227
	E/GiPa	-	-	73.2
	T	-	-	0.236
60NMLCSD #3	VL/ms^{-1}	6923	7392	-
	VS/ms^{-1}	4034	4214	-
	E/GiPa	128.0	139.0	-
	T	0.240	0.259	-
60NMSD #5	VL/ms^{-1}	5681	6594	-
	VS/ms^{-1}	3392	3921	-
	E/GiPa	81.1	107.4	-
	T	0.223	0.226	-
60NMLASD #5	VL/ms^{-1}	6742	7473	6111
	VS/ms^{-1}	4034	4430	3751
	E/GiPa	119.2	145.2	101.5
	T	0.221	0.229	0.198
60NMLASD #6	VL/ms^{-1}	6421	6991	6024
	YS/ms^{-1}	3842	4089	3673
	E/GiPa	104.5	117.3	91.9
	T	0.221	0.240	0.204

VL = Longitudinal velocity VS = Shear velocity E= Young's Modulus
T = Poisson's ratio

PART IV; Young's Modulus of CANMET Produced NASIRPSIO.

The samples received from CANMET were too internally damaged to conduct Young's Modulus measurements.